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Note

THERMOANALYTICAL STUDY OF POTASSIUM NITROSODICYANOMETHANIDE COMPLEX

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A number of thermoanalytical studies (simultaneous T, TG, DTG and DTA) of transition metal nitrosodicyanomethanide complexes have been reported in the literature (see ref. 1, and references therein). However, spectral and electrochemical investigations [1] of the dark yellow crystalline potassium nitrosodicyanomethanide complex have indicated that this complex behaves in a manner different to that of the transition metal nitrosodicyanomethanide complexes. In the present work, the potassium complex was chosen to represent the thermal behaviour of the corresponding group of alkali metal complexes.

EXPERIMENTAL

The experimental method relied on the use of an MOM photorecording derivatograph to register the thermal profiles and follow the thermal behaviour of K(ONC(CN)) in static air and dynamic nitrogen atmospheres. The analysis procedure and instrumental settings were as previously described [1].

Preparation of $K(ONC(CN)_2)$ was based on the method of Köhler and Seifert [2,3]. Oxygen-free nitrogen was obtained by passing the gas through an oxygen-trap train.

RESULTS AND DISCUSSION

Thermal degradation in nitrogen gas

Typical thermal analysis results are shown in Figs. 1 and 2. The complete absence of any weight loss below $T_{max} = 295\,^{\circ}C$ indicates that the sample does not contain any loosely bound or occluded volatile materials such as water or pyridine. Hence the entire loss is due to degradation of

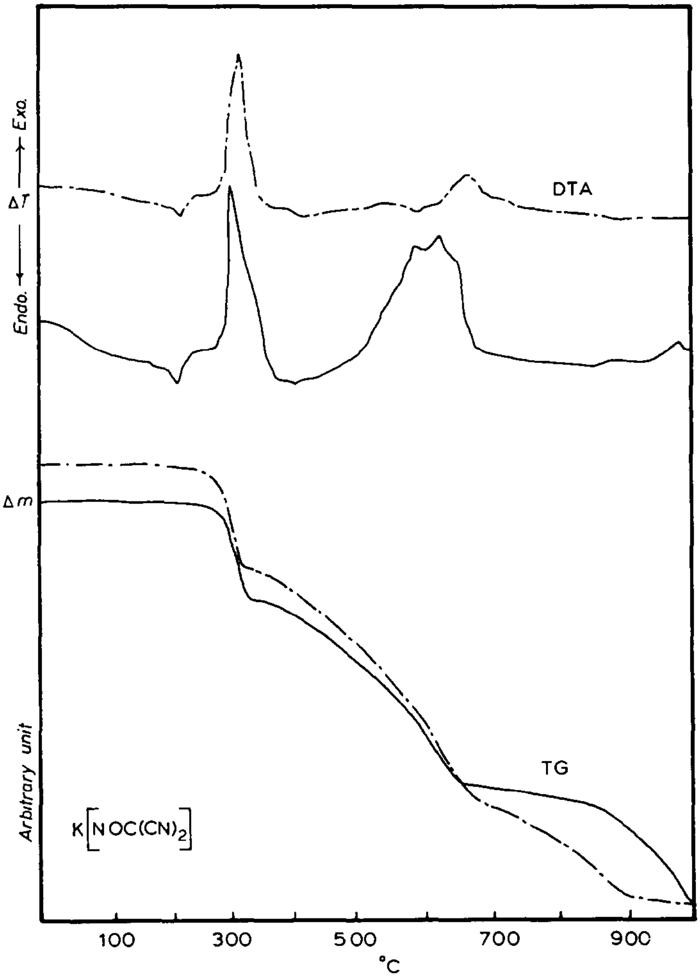

Fig. 1. TG and DTA curves of K[NOC(CN)$_2$] complex: ———, in air; ·———·, in nitrogen.

K(ONC(CN)$_2$). Both the TG and the DTA curves show that this takes place in several stages. Weight loss is rapid (first step) from 230 to 322° C, but less so (second step) from 324 to 710° C. Finally, there is a slow decomposition step over the range 710–933° C. The first decomposition step (238–324° C) is due to the loss of a $\frac{1}{2}$ONC group. TG calculations and evolved gas analysis indicate the simple formation of (CN)$_2$ and nascent oxygen.

$$\mathrm{CNO} \xrightarrow{\Delta} \mathrm{CN} + \mathrm{O} \qquad (1)$$

$$\mathrm{O} + \mathrm{O} \rightarrow \mathrm{O_2} + \text{heat} \qquad (2)$$

$$\mathrm{CN} + \mathrm{O_2} \xrightarrow{\Delta} \mathrm{CO} + \mathrm{NO} + \text{heat} \qquad (3)$$

Hence, the high sharp exotherm appearing at $T_{\max} = 310\,°\mathrm{C}$ is attributable to the two exothermic reactions (2) and (3). The evolution of cyanogen gas

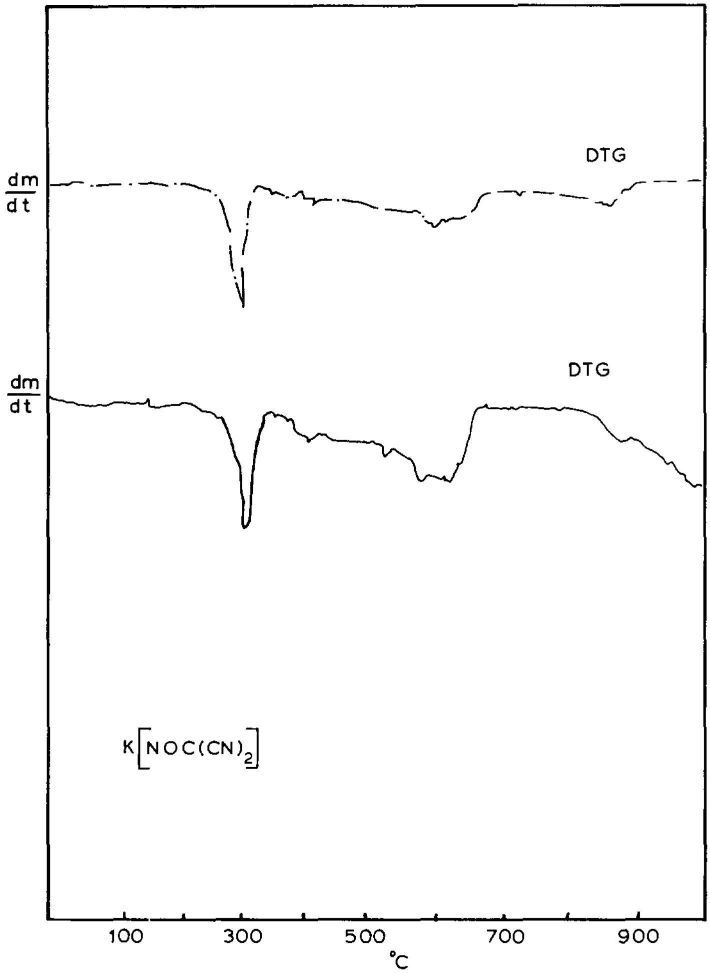

Fig. 2. DTG curves of K(NOC(CN)$_2$) complex: ———, in air; ·———·, in nitrogen.

becomes significant beyond 322 °C, owing to decomposition of the intermediate $(KONC(CN)_2)^-$ [4] (as shown by IR spectrometry). At around 700 °C part of the residual cyanogen is oxidized by traces of oxygen formed as a by-product reaction (2)). Beyond 710 °C the TG curve declines further until 933 °C, owing to decomposition of KONC. There then appears an almost horizontal stretch which corresponds to K_2O (as shown by the powder spectrum in IR). Unexpectedly, potassium carbide is not detected.

The small sharp endotherms at $T_{max} = 200$ °C (in air and nitrogen) represent the melting point endotherms of K(ONC(CN)$_2$), which indicates that decomposition of the complex occurs immediately after melting. This is contrary to behaviour of the transition metal nitrosodicyanomethanide complexes, for which decomposition begins without previous melting.

Thermal degradation in static air

A closely similar pattern of thermal degradation is observed on heating the complex in air, although the three decomposition stages are more defined and the first step, particularly, is highly accentuated (Figs. 1 and 2). Surprisingly, the complex is more stable in air (ambient to 238 ° C) than it is in nitrogen (ambient to 230 ° C). Between 324 and 355 ° C there is an almost imperceptible decomposition of the intermediate $(KONC(CN)_2)^-$, but the loss of cyanogen then increases, and it finishes at 642 ° C. Beyond this there is a more or less horizontal stretch as far as 824 ° C, indicating a very slow decomposition of the resulting KONC (as confirmed by X-ray diffraction patterns and IR spectra). Beyond 824 ° C a sudden collapse of KONC is observed, leading to the evolution and burning of C_2N_2. K_2O is the final product. The corresponding DTG curves suggest that the decomposition of KONC occurs in two overlapping processes ($T_{max} = 860$ and 960 ° C): the first of these is due to loss of oxygen and the second to elimination of $(CN)_2$. The large hump-like exotherm (355–660 ° C) is attributable to the burning of the evolved C_2N_2 gas. The corresponding multistep DTG curves (Fig. 1) confirm that the decomposition of $(KONC(CN)_2)^-$ and the evolution of C_2N_2 are extremely complicated processes.

Thermal decomposition kinetics

The overall apparent activation energy E_a and the pre-exponential factor A for the first decomposition step of the complex under investigation were computed by the Horowitz–Metzger method [5], which uses data from TG and T curves, and Coats–Redfern method [6] for estimation of A. The values computed for E_a and A were 218.3 kJ mol^{-1} and 3.2×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively, over the ranges 238–355 and 230–322 ° C.

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